

On the higher order distribution functions for liquid metals

R. V. GOPALA RAO AND A. K. MURTHY

Physical Chemistry Section, Jadavpur University, Calcutta-700032

(Received 21 January 1976)

Expressions for the isothermal pressure derivatives of the liquid structure factor have been obtained in the $\rho^{-1/3}$ model under the mean spherical model approximation. The theoretical trends for liquid sodium are in good qualitative agreement with the experimental observations for $(\partial S/\partial P)_T$. In the case of mercury it has been found to yield the same set of results over a wide range of pressures (12k bars).

1. INTRODUCTION

The structure of liquids can very well be understood with the language of distribution functions. Egelstaff *et al* (1969, 1971, 1972) have reposed a method of determining the higher order, especially the triplet $g_3(\mathbf{r}, \mathbf{s})$ and quadruplet, $g_4(\mathbf{r}, \mathbf{s}, \mathbf{t})$ distribution functions through the isothermal pressure derivatives of the structure factor, $S(k)$. Recently an expression for the isothermal pressure derivative of $S(k)$ has been obtained in the $\rho^{-1/3}$ model under the mean spherical model (MSM) approximation and the results for liquid rubidium are in good agreement with the experiment (Gopala Rao & Murthy, 1975a, hereafter referred to as I). In this paper it is proposed to extend the same to derive an expression for the second pressure derivative of $S(k)$ and the results for liquid sodium, mercury and rubidium will be discussed.

2. THEORY

The relation between $(\partial S(k)/\partial P)$ and the correction terms, $H(\mathbf{r}, \mathbf{s})$, over the superposition approximation can be written as (Egelstaff *et al* 1971)

$$\rho^2 \int \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \int H(\mathbf{r}, \mathbf{s}) d\mathbf{s} = (2\pi)^{-3} \rho^{-1} [S(k) - 1]^* [S(k) - 1]^2 + [S(k) - 1][S(0) + S(k) - 1] - \rho k_B T \frac{\partial S(k)}{\partial P} \Big|_T = H(k) \quad \dots (1)$$

The second pressure derivative is related to $g_3(\mathbf{r}, \mathbf{s}, \mathbf{t})$ as (Egelstaff & Wang 1972)

$$(\rho k_B T)^2 \left(\frac{\partial^2 S(k)}{\partial P^2} \right) = \rho k_B T \left(\frac{\partial S(k)}{\partial P} \right) \Big|_T + [1 - S(k)] \rho k_B T \left(\frac{\partial S(0)}{\partial P} \right) \Big|_T + [3S(0) - S^2(0)][1 - S(k)] + \rho \int \exp(i\mathbf{k} \cdot \mathbf{r}) d\mathbf{r} \int d\mathbf{s} \rho k_B T \left[\frac{\partial g_3(\mathbf{r}, \mathbf{s})}{\partial P} - \frac{\partial g(\mathbf{s})}{\partial P} - \frac{\partial g(\mathbf{r}, \mathbf{s})}{\partial P} \right] \quad \dots (2)$$

and

$$\rho k_B T \frac{\partial \{\rho^3 g_s(r, s)\}}{\partial P} = \rho^4 \int \{g_s(\mathbf{r}, \mathbf{s}, \mathbf{t}) - g_s(\mathbf{r}, \mathbf{s})\} d\mathbf{t} - 3\rho^3 g_s(\mathbf{r}, \mathbf{s}) \quad \dots \quad (3)$$

The star in eq (1) indicates the convolution

In the $\rho^{-1/3}$ model, the isothermal pressure derivatives of $S(k)$ are given by,

$$\rho k_B T \left(\frac{\partial S(k)}{\partial P} \right)_T = -\frac{k}{3} S^2(0) \left(\frac{\partial S(k)}{\partial k} \right) \quad \dots \quad (4)$$

and

$$(\rho k_B T)^2 \left(\frac{\partial^2 S(k)}{\partial P^2} \right)_T = \frac{k}{9} S^2(0) \left[4 \frac{\partial S(k)}{\partial k} + k \frac{\partial^2 S(k)}{\partial k^2} \right] \quad \dots \quad (5)$$

The details are given in I and the final expression obtained for $(\partial S(k)/\partial P)_T$ under the $\rho^{-1/3}$ model and MSM is,

$$\begin{aligned} \rho k_B T (\partial S(k)/\partial P)_B = & [8S(0)S^2(k)\eta/(k\sigma)^6] \times \\ & \{ \alpha(k\sigma)^3[(k^2\sigma^2 - 3)\sin k\sigma - 3k\sigma \cos k\sigma] + \\ & + \beta(k\sigma)^2[(4k^2\sigma^2 - 8)\cos k\sigma + (k^2\sigma^2 - 8)k\sigma \sin k\sigma + 8] \\ & + \gamma[(k^4\sigma^4 - 12k^2\sigma^2 + 24)6 \cos k\sigma + (k^4\sigma^4 - \\ & - 24k^2\sigma^2 + 144)k\sigma \sin k\sigma - 144] - (\epsilon/k_B T)(k\sigma)^3 \times \\ & \times [(\lambda^2 k^2\sigma^2 - 3)\sin \lambda k\sigma + 3\lambda k\sigma \cos \lambda k\sigma + (3 - k^2\sigma^2) \times \\ & \times \sin k\sigma - 3k\sigma \cos k\sigma] \} \quad \dots \quad (6) \end{aligned}$$

with $\eta = \pi\rho\sigma^3/6$, $\alpha = (1 + 2\eta)^2/(1 - \eta)^4$, $\beta = -6\eta(1 + \eta/2)/(1 - \eta)^4$ and $\gamma = (\eta/2)/(1 + 2\eta)^2/(1 - \eta)^4$

ρ is the average number density, σ the hard sphere diameter and ϵ and λ represent the depth and breadth, respectively, of the square well used

Proceeding as in I, the result for eq (5) follows as,

$$\begin{aligned} (\rho k_B T)^2 \left(\frac{\partial^2 S(k)}{\partial P^2} \right)_T = & -[8S^2(k)S^2(0)\eta/3(k\sigma)^6] \times \\ & \times \{ \alpha(k\sigma)^3[(k^2\sigma^2 - 12)k\sigma \cos k\sigma + (12 - 5k^2\sigma^2) \times \\ & \times \sin k\sigma] + \beta(k\sigma)^2[(k^4\sigma^4 - 20k^2\sigma^2 + 40)\cos k\sigma - \\ & + (20 - 3k^2\sigma^2)2k\sigma \sin k\sigma - 40] + \gamma[(k^4\sigma^4 - \\ & - 42k^4\sigma^4 + 504k^2\sigma^2 - 1008)\cos k\sigma + (-k^4\sigma^4 + \\ & + 21k^2\sigma^2 - 126)8k\sigma \sin k\sigma + 1008] - (\epsilon/k_B T)(k\sigma)^3 \times \\ & \times [(12 - 5\lambda^2 k^2\sigma^2)\sin \lambda k\sigma + (\lambda^2 k^2\sigma^2 - 12)\lambda k\sigma \cos \lambda k\sigma + \\ & + (5k^2\sigma^2 - 12)\sin k\sigma + (12 - k^2\sigma^2)k\sigma \cos k\sigma] - \\ & - (2\rho k_B T/3)(\partial S(k)/\partial P)_T [2S(0) - (3\rho k_B T/S(k)) \times \\ & \times (\partial S(k)/\partial P)_T] \quad \dots \quad (7) \end{aligned}$$

Eqs (6) and (7) are fundamental in character since they relate $(\partial S(k)/\partial P)_T$ and

$(\partial^2 S(k)/\partial P^2)_T$ to the molecular parameters, σ , ϵ and λ . The results for liquid sodium, mercury and rubidium are shown in figures 1 and 3.

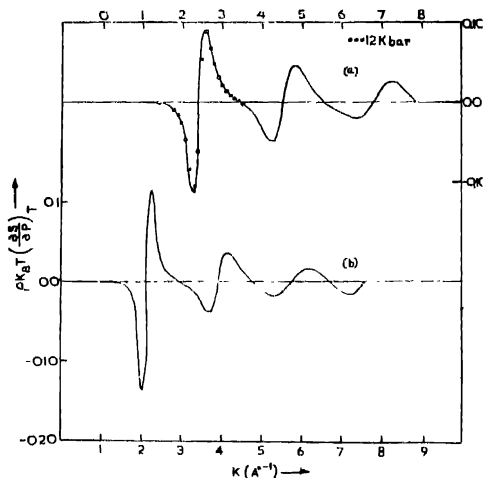


Fig. 1. The isothermal pressure derivative of $S(k)$: (a) mercury at $T = 294.9\text{K}$ and $P = 2\text{ k bars}$ (full line) and $P = -12\text{ k bars}$ (full circles), (b) sodium at $T = 373\text{K}$ and $P = 5\text{ k bars}$.

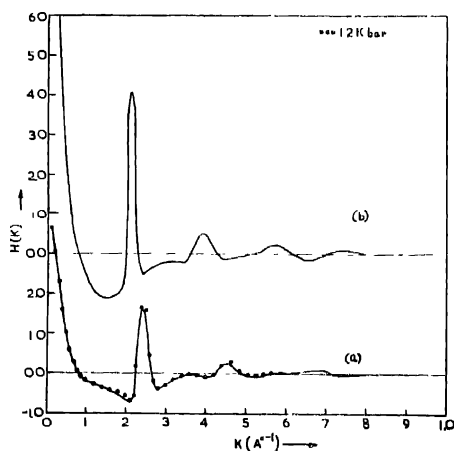


Fig. 2. The function $H(k)$ for the cases (a) and (b) listed in Figure 1.

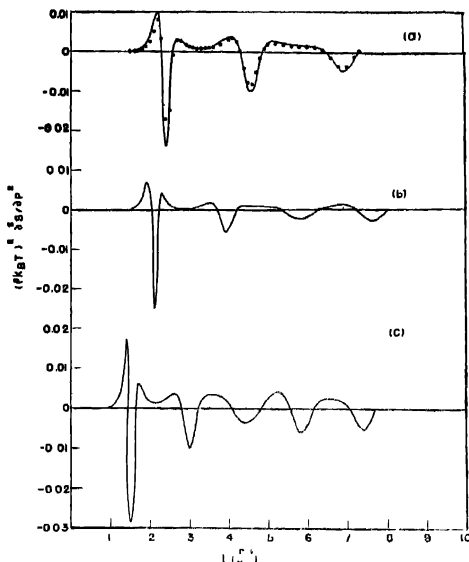


Fig. 3. The isothermal second pressure derivatives of $S(k)$ for the cases (a), (b) listed in Figure 1 (c): rubidium at $T = 333\text{K}$ and $P = 0.43\text{ k bars}$.

3 RESULTS AND DISCUSSION

The parameters σ , ϵ and λ have been determined near the melting temperatures by fitting eq (4) of I with the experimental value at the first peak position (Gopala Rao & Muthly 1975b).

In line with the experimental observations (Wasoda *et al* 1974a) a shift in peak positions of $S(k)$, with increase of pressure by about 0.1Å^{-1} has been observed in all the liquids studied. However, in the case of sodium, the peak height increased by about 15% with an increase of pressure by 5kbars and this has resulted in a high peak in $H(k)$ curve (see Figure 2). In the case of liquid mercury, calculations have been performed over a wide range of pressures (12k bars) and we present our results at $P = 2\text{k bars}$ and at $P = 12\text{k bars}$ in Figures 1-4, as it has been found to yield the same set of values at all other intermediate pressures. Liquid mercury also represents a temperature independent structure (Wasoda *et al* 1974b, Gopala Rao & Muthly 1974).

The minimum in $(\partial S/\partial P)_T$ corresponds to the peak in $S(k)$ curves. Qualitatively the general features of $(\partial S/\partial P)_T$ (for liquid sodium) (Wasoda *et al* 1974) are in good agreement with the experimental observations. Here we could not

conclude quantitatively owing to the lack of experimental (numerical) data. To our knowledge there is no experimental data on $(\partial^2 S/\partial P^2)$ for liquid metals. In the light of the success of this model (Gopala Rao & Murthy 1975b), we believe the present results to be of considerable importance in the absence of experimental data.

The contribution of $(\partial S/\partial P)_T$ and $(\partial^2 S/\partial P^2)_T$ terms to the triplet and quadruplet correlation functions, respectively is quite less. In figure 2 we show the function, $H(k)$ for liquid sodium and mercury and the integral over the isothermal pressure derivative of the triplet correlation (i.e. integral in eq. (3)) for liquid sodium, mercury and rubidium in figure 4. The convolution in eq. (1) has been performed by a Fourier transform technique, taking care to ensure the orthogonality of the discrete sine transforms (Lado 1971).

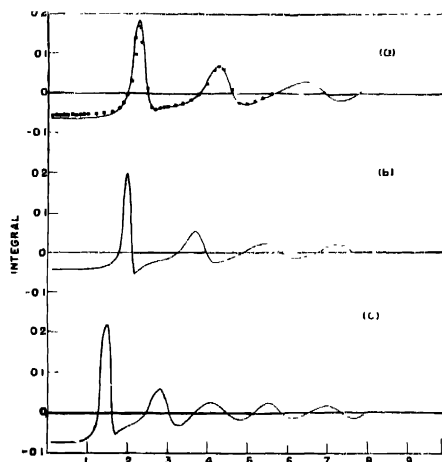


Fig. 4. The integral over $(\delta g_i(\mathbf{r}, \mathbf{s})/\alpha P)_T$ in eq. (2) for the cases listed in Figure 3.

In the calculation of the integral in eq. (2), all the quantities except $(\partial S(0)/\partial P)_T$ are known (eqs. (6) & (7)). Since the $\rho^{-1/3}$ model fails in the limit $k \rightarrow 0$ (see eq. (4) Egelstaff *et al.* 1971) we use an expression for $\partial S(0)/\partial P)_T$, which we obtain within the frame work of MSM as,

$$\rho k_B T \left(\frac{\partial S(0)}{\partial P} \right)_T = S^2(0) \left[1 - \frac{\partial}{\partial P} \left(\frac{1}{\beta T} \right) \right]_T \quad (8)$$

and

$$\frac{\partial}{\partial P} \left(\frac{1}{\beta T} \right) \Big|_T = S(0) \left[\frac{(1 + 2\eta)(1 + 9\eta + 2\eta^2)}{(1 - \eta)^5} - \frac{16\eta\epsilon(\lambda^3 - 1)}{k_B T} \right] \quad \dots \quad (9)$$

where use has been made of the relation,

$$[1/S(0)] = \alpha - 8\eta\epsilon(\lambda^3 - 1)/k_B T \quad \dots \quad (10)$$

which is the result of eq. (4) of I in the limit $k \rightarrow 0$. Here β_T is the isothermal compressibility.

4. CONCLUSIONS

It is worthy to mention that the same set of parameters, fitted to give the correct experimental first peak in $S(k)$ curve, have been used to describe well both equilibrium transport properties of liquid metals (Gopala Rao & Murthy 1975b) and alloys (Gopala Rao & Murthy 1976).

Thus the present theoretical study gives very valuable information regarding the triplet and higher order distribution functions and forms a fundamental approach since it involves the potential parameters only.

ACKNOWLEDGMENT

AKM is grateful to the University Grants Commission for the award of a fellowship during which period this work was done. He is also very much indebted to Dr. Ranjan Datta and to Mr. S. Misra for stimulating this interest in computer programming and also for useful consultations on programming methods.

REFERENCES

- Eglistaff P. A., Page D. I. & Heard C. R. T. 1969 *Phys. Letters* **30A**, 376.
 ———— 1971, *J. Phys. C: Solid St. Phys.* **4**, 1453.
 Eglistaff P. A. & Wang S. S. 1972 *Can. J. Phys.* **50**, 683.
 Gopala Rao R. V. & Murthy A. K. 1974 *Phys. stat. solid (b)* **66**, 703.
 ———— 1975a *Chem. Phys. Letts.* **31**, 605.
 ———— 1975b *E. Naturforsch.* **30a**, 619.
 ———— 1976 *Chem. Phys. Letts* (to appear).
 Lado F. 1971 *J. Computer Phys.* **8**, 417.
 Wasada Y., Ohtani M. & Suzuki K. 1974a, *J. Phys. Chem. Solids* **35**, 585.
 Wasada Y., Yokoyama K. & Suzuki K. 1974b *Phil. Mag.* **29**, 1427.